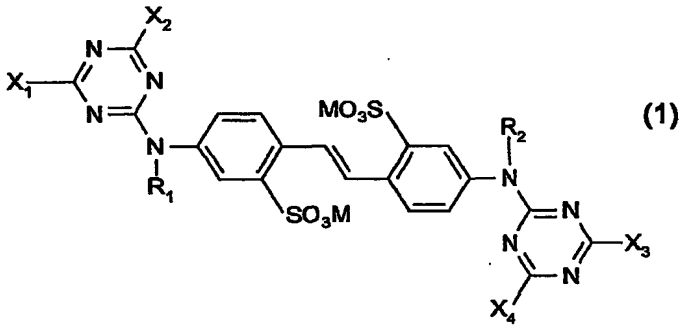
Storage-stable fluorescent whitener formulations

The present invention relates to storage-stable fluorescent whitener formulations, a process for their preparation and their use.

The storage-stable fluorescent whitener formulations according to the invention comprise

(a) 5 – 60% by weight, based on the total weight of the whitener formulation, of at least one compound of formula (1)



(1)

wherein

R_1 and R_2 are, independently from each other, hydrogen; unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl,

X_1, X_2, X_3 and X_4 are, independently from each other, -$N(R_3)R_4$ or -OR_5, wherein

R_3 and R_4 are, independently from each other, hydrogen; cyano; unsubstituted C_1-C_8alkyl; substituted C_1-C_8alkyl; unsubstituted C_5-C_7cycloalkyl or unsubstituted C_5-C_7cycloalkyl; or

R_3 and R_4, together with the nitrogen atom linking them, form a heterocyclic ring, and

R_5 is unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl, and

M is hydrogen or a cation,

(b) 0.01 – 1% by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide,

(c) 0 – 25% by weight, based on the total weight of the whitener formulation, of at least one electrolyte,

(d) 0 – 20% by weight, based on the total weight of the whitener formulation, of at least one dispersant,

(e) 0 – 30% by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener,

(f) 0 – 20% by weight, based on the total weight of the whitener formulation, of at least one further optional component, and

(g) water to make up 100% by weight.

These novel formulations are suspensions, and are stable for several months even at elevated temperatures.

Within the scope of the above definitions, C_1-C_8alkyl may be methyl, ethyl, n- or isopropyl, n-, sec.- or t-butyl, or linear or branched pentyl, hexyl, heptyl or octyl. Preferred are C_1-C_4alkyl groups. In case the alkyl groups are substituted examples of possible substituents are hydroxyl, halogen, like fluorine, chlorine or bromine, sulfo, sulfato, carboxy and C_1-C_4alkoxy, like methoxy and ethoxy. Other substituents of such alkyl groups are, for example, cyano, $-CONH_2$ and phenyl. Preferred substituents are hydroxy, carboxy, cyano, -COOH, $H_2NC(NH)NH_2$, $-CONH_2$ and phenyl, especially hydroxy and carboxy. Furthermore, highly preferred substituents are hydroxy and C_1-C_4alkoxy, especially hydroxy. The alkyl groups can also be uninterrupted or interrupted by –O- (in case of alkyl groups containing two or more carbon atoms).

Examples for C_5-C_7cycloalkyl groups are cyclopentyl and especially cyclohexyl. These groups can be unsubstituted or substituted by, for example, C_1-C_4-alkyl, like methyl. Preferred are the corresponding unsubstituted cycloalkyl groups.

Halogen may be fluorine, chlorine, bromine or iodine, preferably chlorine.

If R_3 and R_4 together with the nitrogen atom form a heterocyclic ring such a ring system can be, for example, morpholino, piperidine or pyrrolidine. The heterocyclic ring can be unsubstituted or substituted. An example for such substituents is C_1-C_4alkyl, especially methyl.

The cation M is preferably an alkali metal cation, an alkaline earth metal cation, ammonium or a cation formed from an amine. Preferred are Li, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C_1-C_4alkylammonium, mono-, di- or tri-C_2-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_2-C_4-hydroxyalkyl groups. Highly preferred is sodium.

R_1 and R_2 are preferably, independently from each other, hydrogen; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl, especially hydrogen.

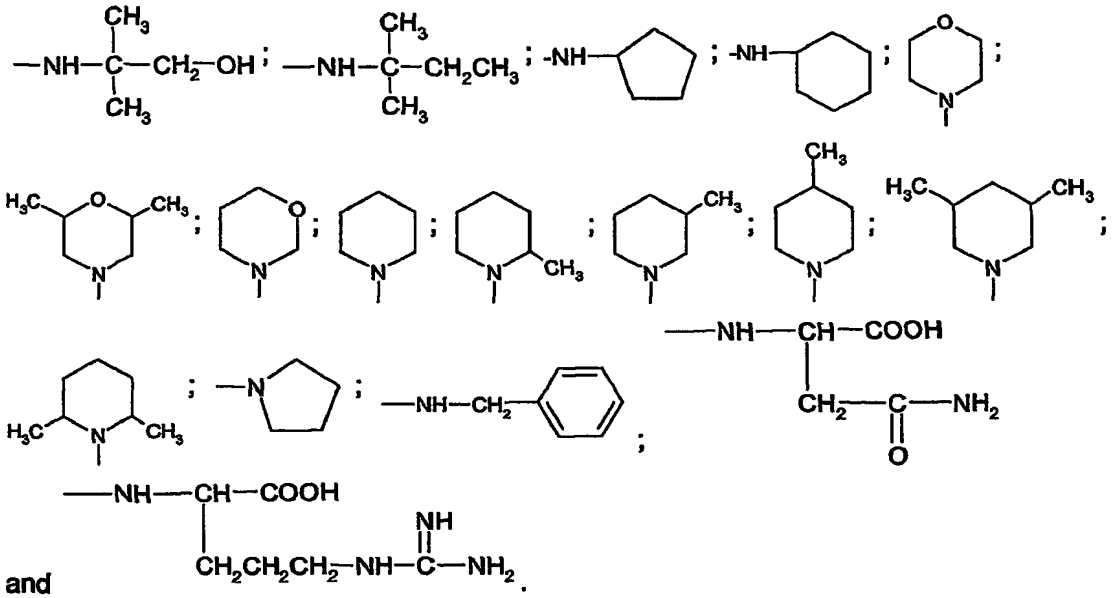
R_3 and R_4 are preferably, independently from each other, hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, cyano, -COOH, $-H_2NC(NH)NH_2$-, $-CONH_2$ or phenyl, especially by hydroxy or carboxy, and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by -O-; unsubstituted or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl, especially cyclohexyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

More preferably, R_3 and R_4 are, independently from each other, hydrogen; unsubstituted C_1-C_8alkyl or hydroxy-substituted C_1-C_8alkyl; unsubstituted C_5-C_7cycloalkyl or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

Most preferred meanings for R_3 and R_4 are, independently from each other, hydrogen; unsubstituted C_1-C_8alkyl or hydroxy-substituted C_1-C_8alkyl; or R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

Highly preferred are unsubstituted morpholino, piperidine or pyrrolidine rings or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine rings, especially morpholino, formed by R_3 and R_4 together with the nitrogen atom linking them.

Examples of $-N(R_3)R_4$ groups are $-NH_2$; $-NHCH_3$; $-NHC_2H_5$; $-NH(n\text{-}C_3H_7)$; $-NH(i\text{-}C_3H_7)$; $-NH(i\text{-}C_4H_9)$; $-N(CH_3)_2$; $-N(C_2H_5)_2$; $-N(i\text{-}C_3H_7)_2$; $-NH(CH_2CH_2OH)$; $-N(CH_2CH_2OH)_2$; $-N(CH_2CH(OH)CH_3)_2$; $-N(CH_3)(CH_2CH_2OH)$; $-N(C_2H_5)(CH_2CH_2OH)$; $-N(i\text{-}C_3H_7)(CH_2CH_2CH_2OH)$; $-NH(CH_2CH(OH)CH_3)$; $-N(C_2H_5)(CH_2CH(OH)CH_3)$; $-NH(CH_2CH_2OCH_3)$; $-NH(CH_2CH_2OCH_2CH_2OH)$; $-NH(CH_2COOH)$; $-NH(CH_2CH_2COOH)$; $-N(CH_3)(CH_2COOH)$; $-NH(CN)$;



and

R_6 is preferably unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl, especially C_1-C_4alkyl, which is unsubstituted or substituted by C_1-C_4alkoxy or especially hydroxy.
Highly preferred for R_5 is methyl or ethyl, especially methyl.

X_1, X_2, X_3 and X_4 are preferably a radical of formula $-N(R_3)R_4$.

X_1 and X_3 have preferably the same meanings. In addition it is preferred that X_2 and X_4 have preferably the same meanings. Furthermore, it is preferred that the four radicals X_1, X_2, X_3 and X_4 do not have identical meanings.

Preferred are compounds of formula (1), wherein
R_1 and R_2 are, independently from each other, hydrogen or unsubstituted C_1-C_4alkyl,
each X_1, X_2, X_3 and X_4 is independently from each other a radical of formula $-N(R_3)R_4$ or OR_5, wherein

R_3 and R_4 are, independently from each other, hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, COOH, cyano, $-CONH_2$, $NHC(NH)NH_2$ or phenyl and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by -O-; unsubstituted C_5-C_7cycloalkyl or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl; or

R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

R_5 is C_1-C_8alkyl which is unsubstituted or substituted by hydroxy.

Highly preferred are compounds of formula (1), wherein

R_1 and R_2 are, independently from each other, hydrogen or unsubstituted C_1-C_4alkyl,

X_1 and X_3 are $-NH_2$, and

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein

R_3 and R_4 are, independently from each other, hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted hydroxy, carboxy, -COOH, cyano, $-CONH_2$, $NHC(NH)NH_2$ or phenyl, and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by -O-; unsubstituted cyclohexyl or C_1-C_4alkyl-substituted cyclohexyl; unsubstituted cyclopentyl or C_1-C_4alkyl-substituted cyclopentyl or

R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

Of particular interest are compounds of formula (1), wherein

R_1 and R_2 are, independently from each other, hydrogen or unsubstituted C_1-C_2alkyl,

X_1 and X_3 are $-NH_2$, and

X_2 and X_4 are a radical of formula $-N(R_3)R_4$, wherein

R_3 and R_4 are, independently of each other, hydrogen; unsubstituted C_1-C_8alkyl or hydroxy-substituted C_1-C_8alkyl; unsubstituted cyclopentyl or C_1-C_4alkyl-substituted cyclopentyl or cyclohexyl; unsubstituted or C_1-C_4alkyl-substituted cyclohexyl; or

R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

Most interesting compounds of formula (1) are those wherein R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring.

The amount of the compound(s) of formula (1) is from 5 to 60% by weight, preferably 5 to 50% by weight, more preferably 10 to 50% by weight, most preferably 10 to 45% by weight, based on the total weight of the whitener formulation.

The compounds of formulae (1) are known or can be prepared in analogy to known processes.

Compounds of formula (1) may be produced by reacting, under known reaction conditions, cyanuric chloride, successively, in any desired sequence, with each of 4,4'-diaminostilbene-2,2'- disulfonic acid, and amino compounds capable of introducing the groups X_1, X_2, X_3 and X_4. Preferably, 2 moles of cyanuric chloride are initially reacted with 1 mole of 4,4'-diaminostilbene-2,2'- disulfonic acid and then reacting the intermediate obtained in any order with amino compounds capable of introducing the groups X_1, X_2, X_3 and X_4. For the preparation of compounds wherein X_1 and X_3 having the same meaning, and also X_2 and X_4 have the same meaning, it is preferred to react the intermediate obtained first with an amino compound capable of introducing X_1 and X_3, and, finally with an amino compound capable of introducing X_2 and X_4. It is also possible to carry out the reaction with the amino compounds in one step by reacting the intermediate with a mixture of amino compounds; in such a case usually corresponding mixtures of compounds of formula (1) are obtained.

Compounds of formula (1) containing a radical of formula $-OR_5$ can for example be prepared by first reacting cyanuric chloride with the corresponding alcohol HOR_5, reacting the product obtained with 4,4'-diaminostilbene-2,2'- disulfonic acid and then reacting the intermediate with further compounds capable of introducing the remaining groups of X_1, X_2, X_3 and X_4. The last reaction is preferably carried out with the corresponding amines.

The anionic polysaccharides which can be used according to the invention belong to the group of modified polysaccharides which can be derived from cellulose, starch or the heteropolysaccharides, it being possible for the side chains to contain further monosaccharides, for example mannose and glucuronic acid. Examples of anionic polysaccharides are sodium alginate, carboxymethylated guar, carboxymethylcellulose, carboxymethyl-starch, carboxymethylated locust bean flour and, particularly preferably, xanthan gum.

The amount of polysaccharide is 0.01 to 1% by weight, a range from 0.05 to 0.5% by weight being preferred and a range of 0.1 to 0.3% by weight being particularly preferred, in each case based on the total weight of the whitener formulation. However, these ranges can be exceeded in formulations of very high concentration or very low concentration.

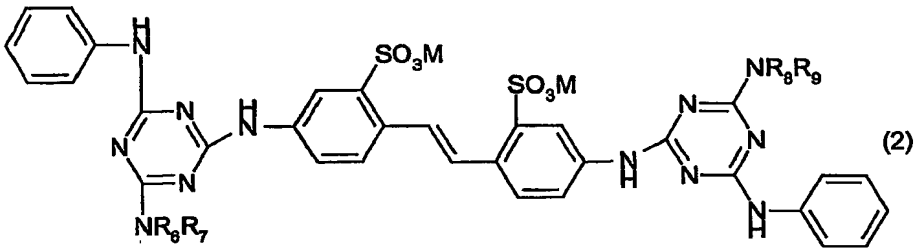
One or more alkali metal salts and salts of lower carboxylic acids, for example, can be used as the electrolyte. Examples of electrolytes are sodium chloride, sodium sulfate, sodium phosphate, sodium carbonate, sodium formate, sodium citrate or one of the corresponding potassium salts, and mixtures of these electrolytes. Sodium chloride, sodium citrate and the formates are preferred here. The amount of electrolyte can be 0 to 25% by weight, preferably 0.5 to 20% by weight and most preferably 0.5 to 15% by weight, based on the total weight of the whitener formulation.

Dispersants which can be used are those of the anionic or nonionic type. Examples of these are alkylbenzenesulfonates, alkyl or alkenyl ether-sulfonate salts, saturated or unsaturated fatty acids, alkyl or alkylene ether-carboxylic salts, sulfo-fatty acid salts or esters, phosphate esters, polyoxyethylene alkyl or alkenyl ethers, polyoxyethylene alkylvinyl ethers, polyoxypropylene alkyl or alkenyl ethers, polyoxybutylene alkyl or alkenyl ethers, higher fatty acid alkanolamides or alkylene oxide adducts, sucrose/fatty acid esters, fatty acid/glycol monoesters, alkylamine oxides and condensation products of aromatic sulfonic acids with formaldehyde, and lignin-sulfonates, or mixtures of the abovementioned dispersants. The condensation products of aromatic sulfonic acids with formaldehyde, and lignin-sulfonates are preferred. Condensation products of naphthalenesulfonic acids with formaldehyde and of ditolyl ether-sulfonic acids with formaldehyde are particularly preferred.

The content of dispersant is 0 to 20% by weight, based on the total weight of the whitener formulation, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, most preferably 0.2 to 5% by weight.

The storage-stable fluorescent whitener formulations according to the invention can further comprise

0 – 30% by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener of formula (2)



(2)

wherein

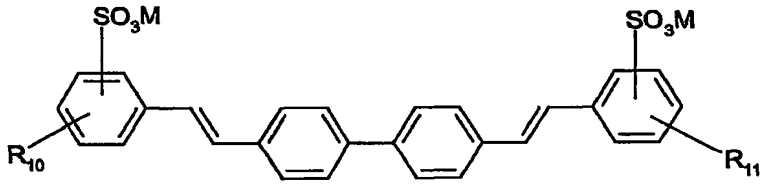
R_6 and R_8, independently from each other, are hydrogen; unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl,

R_7 and R_9, independently from each other, are hydrogen; unsubstituted phenyl; unsubstituted C_1-C_8alkyl or substituted C_1-C_8alkyl, or

NR_6R_7 and/or NR_8R_9 form a morpholino ring,

and M is hydrogen or a cation,

and/or of at least one further fluorescent whitener of formula (3)



(3),

wherein

R_{10} and R_{11}, independently from each other, are hydrogen; substituted C_1-C_8alkyl or unsubstituted C_1-C_8alkyl; C_1-C_8alkoxy or halogen, and M is hydrogen or a cation.

Preferred compounds of formula (2) are those wherein

R_6 and R_8, independently from each other, are hydrogen; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl,

R_7 and R_9, independently from each other, are unsubstituted phenyl; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl, or

NR_6R_7 and/or NR_8R_9 form a morpholino ring,

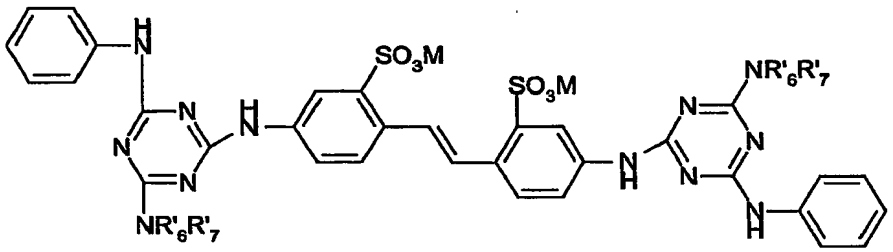
and M is an alkali metal atom, an alkaline earth metal atom, ammonium or a cation formed from an amine.

More preferred compounds of formula (2) are those wherein

R_6 and R_8, independently from each other, are hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,

R_7 and R_9, independently from each other, are unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or
NR_6R_7 and/or NR_8R_9 form a morpholino ring,
and M is an alkali metal atom.

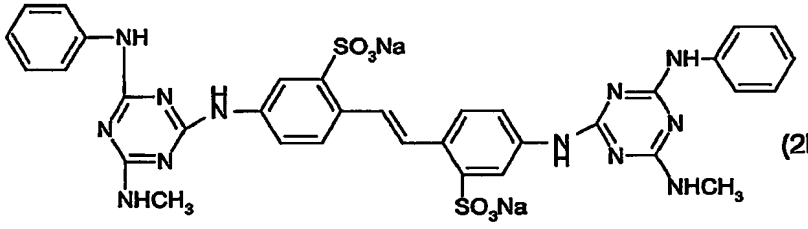
Especially preferred compounds of formula (2) are those of formula (2a)



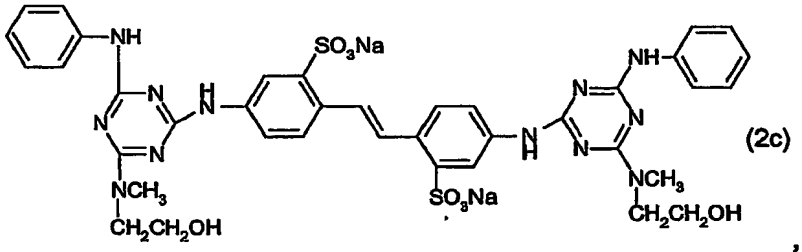
(2a)

wherein
R'_6 is hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,
R'_7 is unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or
$NR'_6R'_7$ forms a morpholino ring,
and M is an alkali metal atom, preferably sodium.

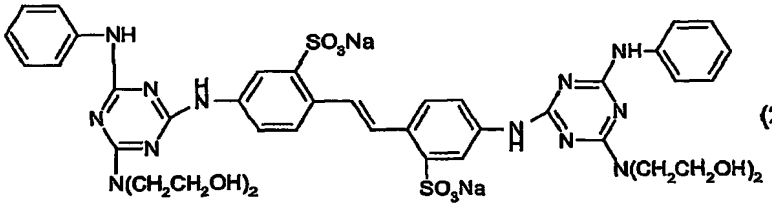
Example of such preferred compounds of formula (2) are those of formula (2b) – (2f)

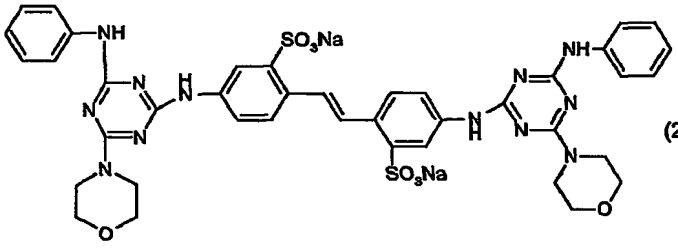


(2b)

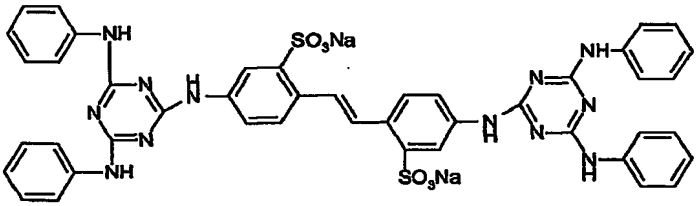


(2c)


(2d)


(2e)

and


(2f)

Preferred compounds of formula (3) are those wherein

R_{10} and R_{11}, independently from each other, are hydrogen; unsubstituted C_1-C_4alkyl or substituted C_1-C_4alkyl; C_1-C_4alkoxy or halogen, and M is hydrogen or a cation.

Compounds of formula (2) and (3) as well as their process of production are known.

In the mixtures of compounds of formulae (1) and (2) and/or (3) the molar ratio of compound (1) to compound (2) and/or compound (3) is usually in the range of from 0.1:99.9 to 99.9:0.1, preferably from 1:99 to 99:1 and more preferably from 5:95 to 95:5. Highly preferred is a molar ratio of from 10:90 to 90:10, especially 20:80 to 80:20. Most important is a molar ratio of from 30:70 to 70:30, especially 40:60 to 60:40.

The content of the further fluorescent whitener(s) is 0 – 30% by weight, based on the total weight of the whitener formulation, preferably 0 to 25% by weight, more preferably 0 to 20% by weight.

If appropriate, the whitener formulation according to the invention can further comprise optional components; examples are preservatives or mixtures of preservatives, such as chloroacetamide, triazine derivates, benzoisothiazolines, 2-methyl-2H-isothiazol-3on, 2-octyl-2H-isothiazol-3on, 2-brom-2-nitropropan-1,3-diol or aqueous formaldehyde solution; Mg/Al silicates or mixtures of Mg/Al silicates, such as bentonite, montmorillonite, zeolites or highly disperse silicic acids; odour improvers and perfuming agent or mixtures thereof; antifoam agents or mixtures thereof; builders or mixtures thereof; protective colloids or mixtures thereof; stabilizers or mixtures thereof; sequestering agents and antifreeze agents or mixtures thereof, such as propylene glycol.

The content of these optional components is 0 to 20% by weight, based on the total weight of the whitener formulation, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, most preferably 0.2 to 5% by weight.

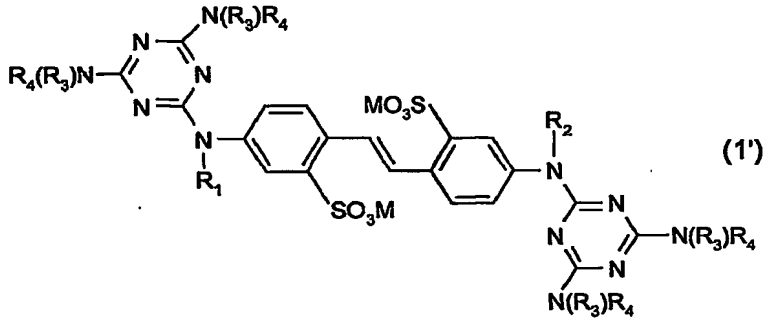
Examples of suitable builders or protective colloids are modified polysaccharides derived from cellulose or heteropolysaccharides, such as xanthan gum, carboxymethylcellulose and polyvinyl alcohols (PVA), polyvinylpyrrolidones (PVP), polyethylene glycols (PEG) and aluminium silicates or magnesium silicates. They are usually used in a concentration range of 0.01 to 2% by weight and preferably 0.05 to 0.5% by weight, based on the total weight of the whitener formulation.

Examples of auxiliaries which can be used for stabilization are ethylene glycol, propylene glycol or dispersants in an amount of 0.2 to 5% by weight and preferably 0.3 to 2% by weight, based on the total weight of the whitener formulation.

Compounds which are used as preservatives are chloroacetamide, triazine derivates, benzoisothiazolines, 2-methyl-2H-isothiazol-3on, 2-octyl-2H-isothiazol-3on, 2-brom-2-nitropropan-1,3-diol or aqueous formaldehyde solution in an amount of 0.1 to 1% by weight and preferably 0.1 to 0.5% by weight based on the total weight of the whitener formulation.

A preferred storage-stable fluorescent whitener formulation according to the invention comprises

(a) 5 – 50% by weight, preferably 10 – 50% by weight, more preferably 10 – 45% by weight, based on the total weight of the whitener formulation, of at least one compound of formula (1')



(1')

wherein

R_1 and R_2 are, independently from each other, hydrogen or unsubstituted C_1-C_4alkyl,

R_3 and R_4 are, independently from each other, hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, -COOH, $-H_2NC(NH)NH_2$, cyano, $-CONH_2$ or phenyl and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by -O-; unsubstituted C_5-C_7cycloalkyl or C_1-C_4alkyl-substituted C_5-C_7cycloalkyl; or

R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

M is an alkali metal cation; an alkaline earth metal cation; ammonium or a cation formed from an amine,

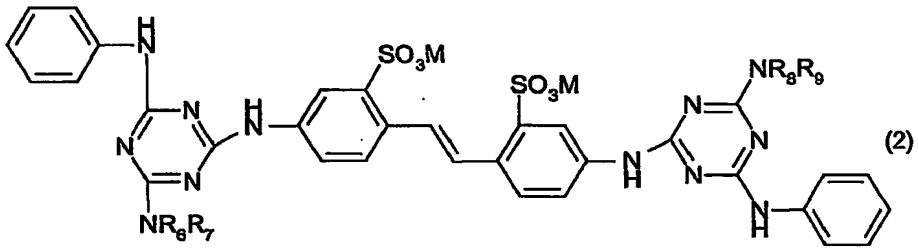
(b) 0.05 – 0.5% by weight, preferably 0.1 – 0.3% by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide,

(c) 0 – 25% by weight, preferably 0.5 – 20% by weight, more preferably 0.5 – 15% by weight, based on the total weight of the whitener formulation, of at least one electrolyte from the group consisting of alkali metal salts and/or lower carboxylic acids,

(d) 0 – 20% by weight, preferably 0.1 – 20% by weight, more preferably, 0.1 – 10% by weight, especially preferred 0.2 – 5% by weight, based on the total weight of the whitener formulation, of at least one dispersant from the group consisting of alkylbenzenesulfonates; alkyl or alkenyl ether-sulfonate salts; saturated or unsaturated fatty acids; alkyl or alkylene ether-carboxylic salts; sulfo-fatty acid salts or esters; phosphate esters; polyoxyethylene alkyl or alkenyl ethers; polyoxyethylene alkylvinyl

ethers; polyoxypropylene alkyl or alkenyl ethers; polyoxybutylene alkyl or alkenyl ethers; higher fatty acid alkanolamides or alkylene oxide adducts; sucrose/fatty acid esters; fatty acid/glycol monoesters; alkylamine oxides and condensation products of aromatic sulfonic acids with formaldehyde; and lignin-sulfonates,

(e) 0 – 30% by weight, preferably 0 – 25% by weight, more preferably 0 – 20% by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener from the group consisting of compounds of formula (2)



(2)

wherein

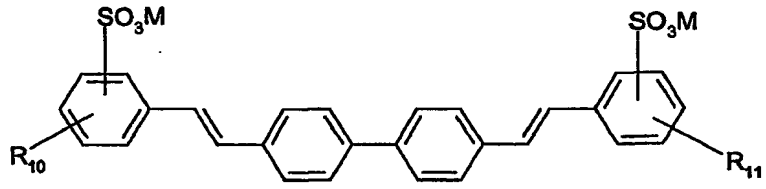
R_6 and R_8, independently from each other, are hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,

R_7 and R_9, independently from each other, are unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or

NR_6R_7 and/or NR_8R_9 form a morpholino ring, and

M is an alkali metal atom,

and compounds of formula (3)



(3),

wherein

R_{10} and R_{11}, independently from each other, are hydrogen; C_1-C_4alkyl; C_1-C_4alkoxy or halogen, and M is hydrogen or a cation,

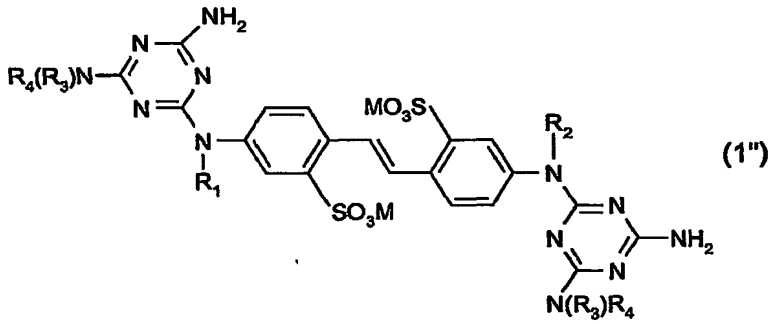
(f) 0 – 20% by weight, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, most preferably 0.2 to 5% by weight based on the total weight of the whitener formulation, of at least one further optional component from the group consisting of preservatives; Mg/Al silicates; odour improvers and perfuming agent; builder or protective colloids; stabilizers; sequestering agents and antifreeze agents,

(g) water to make up 100% by weight.

A more preferred storage-stable fluorescent whitener formulations according to the invention comprises

(a) 10 – 50% by weight, preferably 10 – 45% by weight, based on the total weight of the whitener formulation, of at least

one compound of formula (1")



(1")

wherein

R_1 and R_2 are, independently from each other, hydrogen; methyl or ethyl,

R_3 and R_4 are, independently from each other, hydrogen; cyano; C_1-C_8alkyl which is unsubstituted or substituted by hydroxy, carboxy, -COOH, -$CONH_2$, $H_2NC(NH)NH_2$, phenyl and wherein the C_1-C_8alkyl group is uninterrupted or interrupted by -O-; unsubstituted C_5-C_7cyclohexyl or C_1-C_4alkyl-substituted C_5-C_7cyclohexyl; or

R_3 and R_4, together with the nitrogen atom linking them, form an unsubstituted morpholino, piperidine or pyrrolidine ring or a C_1-C_4alkyl-substituted morpholino, piperidine or pyrrolidine ring; and

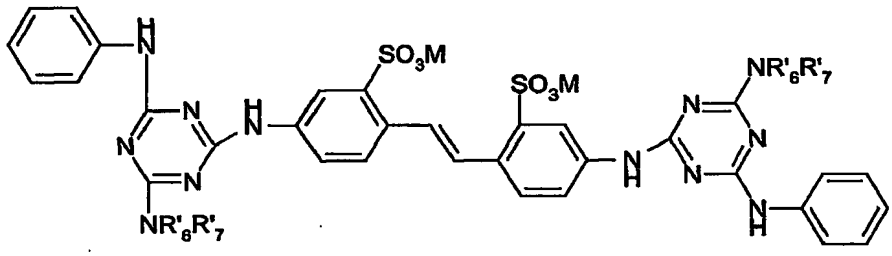
M is Li; Na; Ca; Mg; ammonium; mono-, di-, tri- or tetra-C_1-C_4alkylammonium; mono-, di- or tri-C_2-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_2-C_4-hydroxyalkyl groups,

(b) 0.05 – 0.5% by weight, preferably 0.1 – 0.3% by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide from the group consisting of sodium alginate; carboxymethylated guar; carboxymethylcellulose; carboxymethyl-starch; carboxymethylated locust bean flour and xanthan gum,

(c) 0 – 25% by weight, preferably 0.5 – 20% by weight, more preferably 0.5 – 15% by weight, based on the total weight of the whitener formulation, of at least one electrolyte from the group consisting of sodium or potassium chloride; sodium or potassium sulfate; sodium or potassium phosphate; sodium or potassium carbonate; sodium or potassium formate; sodium or potassium citrate,

(d) 0 – 20% by weight, preferably 0.1 – 20% by weight, more preferably, 0.1 – 10% by weight, especially preferred 0.2 – 5% by weight, based on the total weight of the whitener formulation, of at least one dispersant from the group consisting of alkylbenzenesulfonates; alkyl or alkenyl ether-sulfonate salts; saturated or unsaturated fatty acids; alkyl or alkylene ether-carboxylic salts; sulfo-fatty acid salts or esters; phosphate esters; polyoxyethylene alkyl or alkenyl ethers; polyoxyethylene alkylvinyl ethers; polyoxypropylene alkyl or alkenyl ethers; polyoxybutylene alkyl or alkenyl ethers; higher fatty acid alkanolamides or alkylene oxide adducts; sucrose/fatty acid esters; fatty acid/glycol monoesters; alkylamine oxides and condensation products of naphthalene sulfonic acids with formaldehyde; and lignin-sulfonates,

(e) 0 – 25% by weight, more preferably 0 – 20% by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener from the group consisting of compounds of formula (2a)



(2a)

wherein

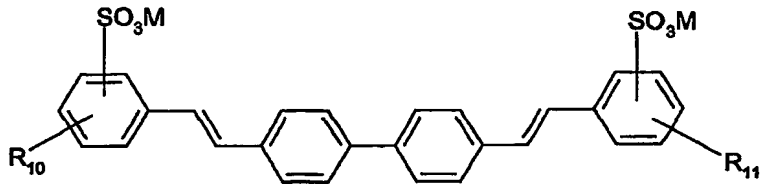
R'_6 is hydrogen; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy,

R'_7 is unsubstituted phenyl; unsubstituted C_1-C_2alkyl or C_1-C_4alkyl, which is substituted by hydroxy or C_1-C_4alkoxy, or

$NR'_6R'_7$ forms a morpholino ring,

and M is an alkali metal atom, preferably sodium,

and compounds of formula (3)



(3),

wherein

R_{10} and R_{11}, independently from each other, are hydrogen; C_1-C_2alkyl; C_1-C_2alkoxy; Cl or Br, and

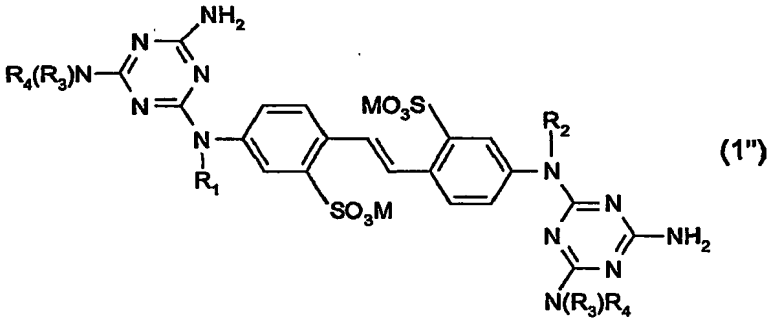
M is hydrogen or an alkali metal atom, preferably sodium,

(f) 0 – 20% by weight, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, particularly preferably 0.2 to 5% by weight based on the total weight of the whitener formulation, of at least one further optional component from the group consisting of chloroacetamide; triazine derivates; benzoisothiazolines; 2-methyl-2H-isothiazol-3on; 2-octyl-2H-isothiazol-3on; 2-brom-2-nitropropan-1,3-diol; aqueous formaldehyde solution; bentonite; montmorillonite; zeolites; polyvinyl alcohols (PVA), polyvinylpyrrolidones (PVP), polyethylene glycols (PEG); aluminium silicates; magnesium silicates; ethylene glycol and propylene glycol ,

(g) water to make up 100% by weight.

An especially preferred storage-stable fluorescent whitener formulation according to the invention comprises

(a) 10 – 45% by weight, based on the total weight of the whitener formulation, of at least one compound of formula (1")

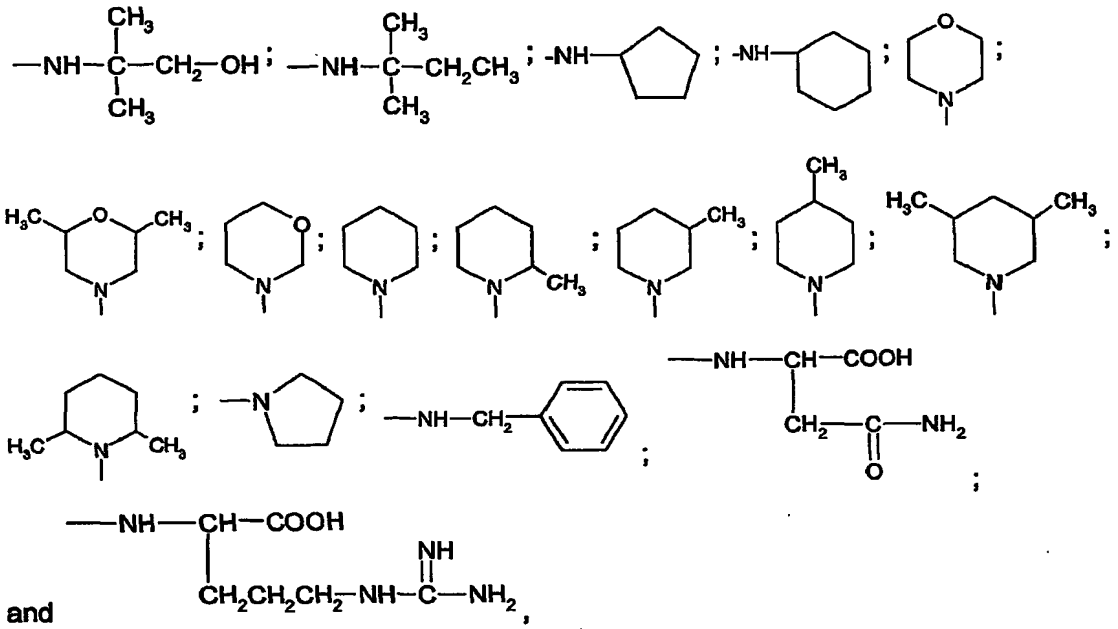


(1")

wherein

R_1 and R_2 are, independently from each other, hydrogen; methyl or ethyl,

R_3 and R_4 are, independently from each other, $-NH_2$; $-NHCH_3$; $-NHC_2H_5$; $-NH(n\text{-}C_3H_7)$; $-NH(i\text{-}C_3H_7)$; $-NH(i\text{-}C_4H_9)$; $-N(CH_3)_2$; $-N(C_2H_5)_2$; $-N(i\text{-}C_3H_7)_2$; $-NH(CH_2CH_2OH)$; $-N(CH_2CH_2OH)_2$; $-N(CH_2CH(OH)CH_3)_2$; $-N(CH_3)(CH_2CH_2OH)$; $-N(C_2H_5)(CH_2CH_2OH)$; $-N(i\text{-}C_3H_7)(CH_2CH_2CH_2OH)$; $-NH(CH_2CH(OH)CH_3)$; $-N(C_2H_5)(CH_2CH(OH)CH_3)$; $-NH(CH_2CH_2OCH_3)$; $-NH(CH_2CH_2OCH_2CH_2OH)$; $-NH(CH_2COOH)$; $-NH(CH_2CH_2COOH)$; $-N(CH_3)(CH_2COOH)$; $-NH(CN)$;



and

M is Li; Na; Ca; Mg; ammonium; mono-, di-, tri- or tetra-C_1-C_4alkylammonium; mono-, di- or tri-C_2-C_4-hydroxyalkylammonium or ammonium that is di- or tri-substituted with a mixture of C_1-C_4-alkyl and C_2-C_4-hydroxyalkyl groups,

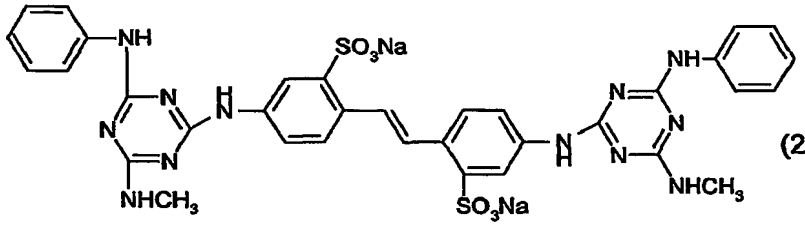
(b) 0.05 – 0.5% by weight, preferably 0.1 – 0.3% by weight, based on the total weight of the whitener formulation, of at least one anionic polysaccharide from the group consisting of sodium alginate; carboxymethylated guar; carboxymethylcellulose; carboxymethyl-starch; carboxymethylated locust bean flour and xanthan gum,

(c) 0 – 25% by weight, preferably 0.5 – 20% by weight, more preferably 0.5 – 15% by weight, based on the total weight of the whitener formulation, of at least one electrolyte from the group consisting of sodium or potassium chloride; sodium or potassium sulfate; sodium or potassium phosphate; sodium or potassium carbonate; sodium or potassium formate; sodium or potassium citrate,

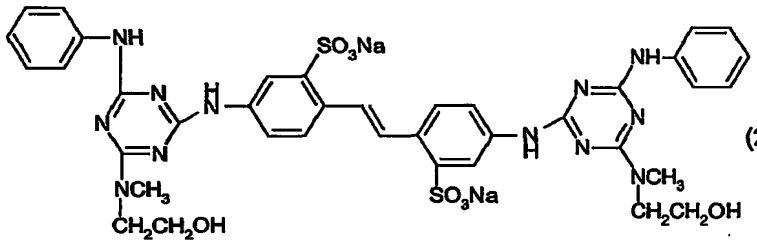
(d) 0 – 20% by weight, preferably 0.1 – 20% by weight, more preferably, 0.1 – 10% by weight, most preferably 0.2 – 5% by weight, based on the total weight of the whitener formulation, of at least one dispersant from the group consisting of alkylbenzenesulfonates; alkyl or alkenyl ether-sulfonate salts; saturated or unsaturated fatty acids; alkyl or alkylene ether-carboxylic salts; sulfo-fatty acid salts or esters; phosphate esters; polyoxyethylene alkyl or alkenyl ethers; polyoxyethylene alkylvinyl ethers; polyoxypropylene alkyl or alkenyl ethers; polyoxybutylene alkyl or alkenyl ethers; higher fatty acid alkanolamides or alkylene oxide adducts; sucrose/fatty acid

esters; fatty acid/glycol monoesters; alkylamine oxides and condensation products of naphthalene sulfonic acids with formaldehyde; and lignin-sulfonates,

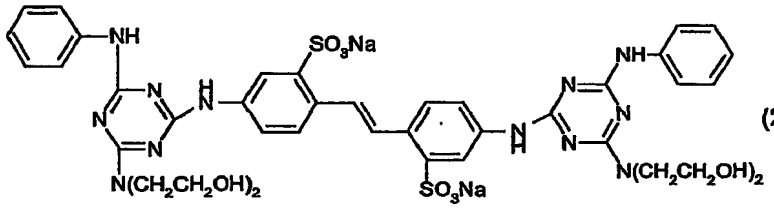
(e) 0 – 25% by weight, more preferably 0 – 20% by weight, based on the total weight of the whitener formulation, of at least one further fluorescent whitener from the group consisting of compounds of formula



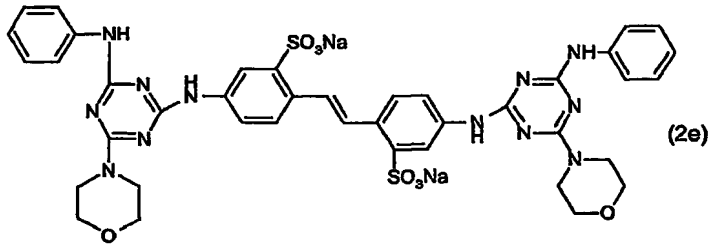
(2b)



(2c)

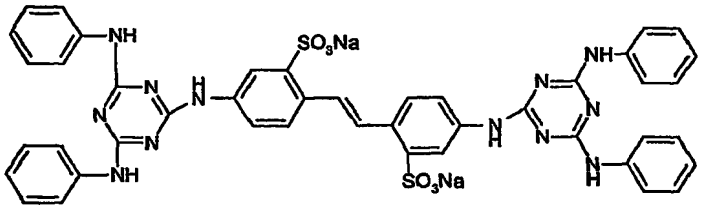


(2d)



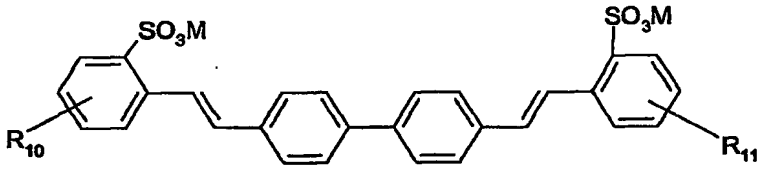
(2e)

and



(2f)

and compounds of formula (3')



(3'),

wherein

R_{10} and R_{11}, independently from each other, are hydrogen; C_1-C_2alkyl; C_1-C_2alkoxy; Cl or Br, and

M is hydrogen or an alkali metal atom, preferably sodium,

(f) 0 – 20% by weight, preferably 0.1 to 20% by weight, more preferably 0.1 to 10% by weight, particularly preferably 0.2 to 5% by weight based on the total weight of the whitener formulation, of at least one further optional component from the group consisting of chloroacetamide; triazine derivates; benzoisothiazolines; 2-methyl-2H-isothiazol-3on; 2-octyl-2H-isothiazol-3on; 2-brom-2-nitropropan-1,3-diol; aqueous formaldehyde solution; bentonite; montmorillonite; zeolites; polyvinyl alcohols (PVA), polyvinylpyrrolidones (PVP), polyethylene glycols (PEG); aluminium silicates; magnesium silicates; ethylene glycol and propylene glycol ,

(g) water to make up 100% by weight.

The storage-stable formulations of this invention are prepared by mixing the moist filter cake or also the dry powder, which comprises at least one fluorescent whitening agent of formula (1) in an amount of 5 - 60% by weight, based on the total weight of the formulation, with 0.01-1% by weight of an anionic polysaccharide and water, and homogenising the formulations.

The desired content of anionic fluorescent whitening agent in the suspension can be adjusted either by addition of water, aqueous electrolyte, suspension, further fluorescent agent(s) of formulae (2) and/or (3) or further dry powder to the moist filter cake. This adjustment can be made before, during or after addition of the anionic polysaccharide.

The concentrated formulation thus prepared can be used for the fluorescent whitening of paper or textile material, for example in detergents. To this end, they are in general diluted to the optimum concentration for the practical application by the addition of further components or water.

The novel storage-stable fluorescent whitener formulations are used in particular for incorporation into washing agents, for example by allowing the required amount of the fluorescent whitener formulation according to the invention to run from a tank into a mixing device which contains a suspension of the washing agent or the dispersant.

It is also possible to prepare a solid form of the formulation according to the present invention. Such a solid formulation can be prepared according to conventional methods, such as for example spray drying.

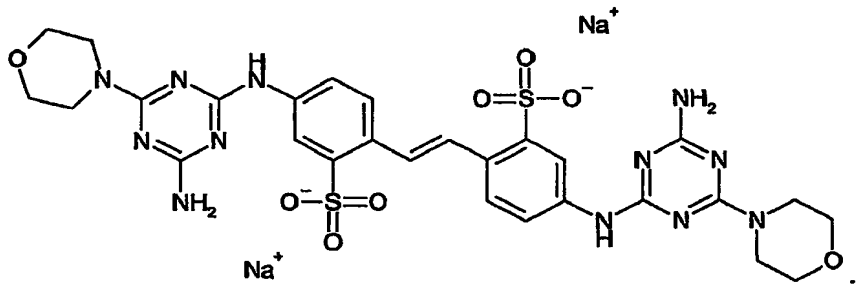
The present invention accordingly also relates to a process for the preparation of solid and liquid washing agents, and to the washing agents obtained by this process, which comprises mixing, for example, a suspension of detergents customary for washing agents with a suspension, according to the invention, of whiteners, and drying the mixture. The drying procedure here can be carried out by, for example, a spray-drying method.

The following examples illustrate the invention, without limiting it thereto. Percentage data relate to the total weight of the formulation.

EXAMPLE 1

With stirring, the components listed below are mixed and homogenised at 20°C:

30.0% by weight of the fluorescent whitening agent of formula



;

0.5% by weight of propylene glycol;

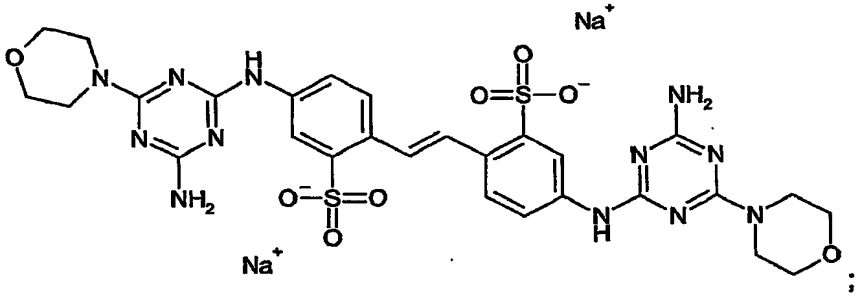
0.25% by weight of Xanthan,

0.4% by weight of Acticide MBS® (Trade name of Acti-Chem Specialties Inc.) and deionised water to make up 100%.

EXAMPLE 2

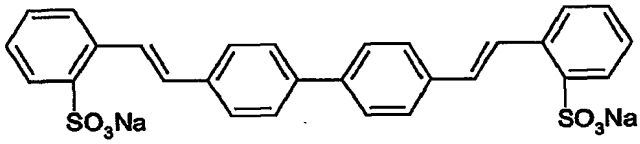
With stirring, the components listed below are mixed and homogenised at 20°C:

11.1% by weight of the fluorescent whitening agent of formula



;

18.9% by weight of the fluorescent whitening agent of formula



0.5% by weight of propylene glycol;

0.25% by weight of Xanthan,

0.4% by weight of Acticide MBS® (Trade name of Acti-Chem Specialties Inc.)

0.001% by weight of Surfynol 104 PG 50® (Trade name of Air Products and Chemicals Inc.) and deionised water to make up 100%.